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Fabrication and Characterization of Pt doped Ti/Sb-SnO_2 Electrode and its Efficient Electro-Catalytic Activity toward Phenol

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Abstract

An optimized metal oxide electrode was prepared via the simple thermal decomposition method to improve the stability and electro-catalytic properties. It was found that Pt doping could effectively change the surface morphology. The Ti/Pt-Sb-SnO_2 electrode possess compact and uniform surface packed with a large number of small particles. Besides, the influence of the Pt on the electrochemical performance was analyzed in detail. The oxygen evolution potential of Ti/Pt-Sb-SnO_2 electrode decreased slightly, but it showed a smaller charge transfer resistance (0.2 $\Omega\cdot cm^2$ versus 1.67 $\Omega\cdot cm^2$) and a longer service lifetime which is almost 24-times longer than that of Ti/Sb-SnO_2 (73 h versus 3h). Finally, electro-catalytic oxidation of phenol was employed. In the electro-catalytic process, both phenol and its possible intermediates were more rapidly decomposed on the Ti/Pt-Sb-SnO_2 electrodes. The removal of chemical oxygen demand（COD) was 95.56% and 56.31% on the Ti/Pt-Sb-SnO_2 and Ti/Sb-SnO_2 electrodes, respectively. And the corresponding instantaneous current efficiency (ICE) of Ti/Pt-Sb-SnO_2 electrode was higher than that of Ti/Sb-SnO_2. Based on the experimental results, the prepared Ti/Pt-Sb-SnO_2 electrode has better stability and excellent phenol electro-catalytic ability, further signifying that it has a good potential application prospect in the field of wastewater.

Keywords: $Ti_3C_2T_x$ MXene film; Microgel; Super-fast preparation; Good electrical conductivity; High volumetric capacitance.
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1. Introduction

In recent years, titanium-based metal oxide anodes as promising materials have been widely used in many fields, such as organic electro-synthesis, water electrolysis, electronic device and electro-catalytic degradation of organic pollutants.[1-8] Up to date, a large number of metal oxide electrodes have been studied, including ruthenium oxide (RuO_2), iridium oxide (IrO_2), lead oxide (PbO_2), tin oxide (SnO_2) and so on.[9-15] It is well known that the performance of metal oxide active coatings, such as the chemical composition, the structure, the morphology and so on, which play vital role in the electro-catalytic properties. It not only affects the reaction rate, reaction selectivity, reaction mechanism and the path of electrochemical reactions, but also directly determines the success or failure of electrochemical reaction. In the electrochemical process, oxygen evolution reaction (OER) is an inevitable side reaction, which will cause an unwanted power loss and ultimately reduce the overall current efficiency. Therefore, anode material with a high oxygen evolution potential (OEP) is especially desirable since high OEP is conducive to the oxidation of organic pollutants on the electrode surface, which can effectively inhibit the occurrence of OER, decrease the unwanted power loss and improve the overall current efficiency.[16-18]

The Ti/Sb-SnO_2 electrodes is considered to be one of the most attractive alternatives for the electro-catalytic of organic contaminants due to high OEP, easy preparation, high electrical conductivity, low cost, no secondary pollution and excellent electro-catalytic ability (good ability to generate OH·).[1,16-21] Yao *et al.* investigated the effects of Sb doping level on the properties of the Ti/Sb-SnO_2 electrodes. He also found that the crystal size, microstructure, resistivity, electrochemical behavior and electro-catalytic activity for pollutant oxidation were highly dependent on the doping level

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and 3% Sb-doped electrodes have the lowest resistivity and best electro-catalytic activity.[16] We previously investigated the Sb-doped Ti/SnO_2 anodes by magnetron sputtering technology. The high OEP was gained, which is about 2.2-2.3 eV. The effects of annealing temperatures on the physical and electrochemical properties of the electrodes were also studied.[17] Dongwook Lim *et al*. examined the effect of the doping amount on the electrochemical activity and stability of the electrode. They found that the Ti/SnO_2 electrode with 10% Sb dopant showed the highest catalytic activity and COD removal (87%). They suggested that the Ti/SnO_2 electrode with an optimized Sb dopant amount shows enhanced electro-catalytic performance by easily generating active hydroxyl radicals, which acts as strong oxidizing agents.[18] Soonhyun Kim *et al*. prepared Ti/RuO_2 and Ti/Sb-SnO_2 electrodes and investigated their electrocatalytic activities. They found that the Ti/Sb-SnO_2 have more superiority over Ti/RuO_2 for degrading the pollutants.[21] Shao *et al*. compared the performances of Ti/Sb-SnO_2 and Ti/PbO_2 electrodes by evaluating the change of COD and UV-Vis absorption showing that the Ti/Sb-SnO_2 exhibited a higher pollutant and COD removal efficiency.[22] Although the Ti/Sb-SnO_2 electrode has been widely studied in the field of electro-catalysis, its relative short life (poor stability) is the most important issue limiting its practical application severely. In addition, the electro-catalytic activity of the Ti/SnO_2-Sb electrodes is not sufficient yet and there's still a lot of space for improvement. Therefore, a great deal of efforts, such as ion doping, intermediate layer insertion and modification of Ti substrate, have been devoted to surmounting this weakness.[23-36] Remarkably, the ions doping (co-doped X-Sb-SnO_2 electrodes, X represents Mn, Au, Pt, Ni, rare earth and so on) are one expected and effective strategy. A series of studies on the Ti/X-Sb-SnO_2 electrodes have been carried out.[9,28,33-35,37-43]

In recent years, our group has also conducted studies on different metal ion doping. These metals can not only effectively change the concentration of oxygen vacancies in the SnO_2 crystal lattice, but also influence the electro-catalytic performance of electrodes.[28,29,33-35] For examples, we studied the Mn-Sb and Cr-Sb co-doped Ti/Sb-SnO_2 electrodes with a range of physicochemical and electrochemical treatments.[28,29] The Ti/Mn-Sb-SnO_2 electrode presented the most stable electro-catalytic activity and the lowest resistance. Moreover, it showed significant improvement in the service life of electrode, which was almost 7 times longer than that of Ti/Sb-SnO_2 electrode. We also studied the effect of Ni doping on electrode performance in detail. Results showed that the Ti/Sb-SnO_2 electrode doped with Ni had a superior electrical conductivity and a high oxygen evolution potential.[35]

It is well known that Pt is a chemically stable material with excellent catalytic property, which is expected to improve the performance of Ti/Sb-SnO_2 electrodes effectively used as a doping element from an electrochemical and physicochemical point of view. Recently, some researchers have studied the Ti/Sb-SnO_2 anodes by introducing a small amount of Pt (Ti/Pt-Sb-SnO_2 anodes), which can improve the performance of Ti/Sb-SnO_2 electrodes effectively. These results further confirmed that the incorporation of trace amounts of Pt have a great impact on the electrochemical properties and significantly improve the electrode stability, which are mainly due to the compacting effect of Pt.[44-54] F. Montilla *et al*. studied the effect of Pt on the physical and electrochemical properties of the electrode in detail. They found that the introducing Pt modifies the lattice parameters and morphology of the SnO_2 effectively. The number of the cracks in the coating is significantly reduced and the service life of electrodes has been increased in several orders of magnitude ultimately, as previously reported. Ti/Pt-Sb-SnO_2 electrode also showed an even higher efficiency for phenol electro-oxidation.[45-50,52,54] F. Vicent *et al*. found that the surface of Ti/Pt-Sb-SnO_2 electrode presents a uniform distribution of particles. In addition, the stability of Pt doped SnO_2 electrodes increased significantly.[44] A.I. del Río *et al*. also confirmed that the presence of platinum in the Ti/SnO_2-Sb-Pt anodes contributes to a more compact morphology, which is useful for wastewater treatment and the stability of electrode.[51] Detail structure properties and electrochemical analysis, as well as the electro-catalytic performance of Pt modifying, are still needed to further investigated.

Thus, the primary aim of our study was to improve the performance of the Ti/Sb-SnO_2 electrode through doping with Pt. In this work, we attempted to prepare a novel metal oxide electrode with Pt-Sb co-doped. Then we investigated the influence of Pt doping on the physical and electro-catalytic performance of Ti/Pt-Sb-SnO_2 electrodes in detail. In addition, to further examine the electro-catalytic performance of Ti/Pt-Sb-SnO_2 electrodes, phenol was chosen as a representative pollutant. And the electro-catalytic activity of the anodes was evaluated by the COD removal.

2. Materials and methods

2.1 Electrode preparation

2.1.1 Chemical reagents

The reagents we used included tin chloride (II) ($SnCl_2{\cdot}5H_2O$, AR), antimony chloride (III) ($SbCl_3$, AR) and chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, AR), ethyl alcohol (C_2H_5OH, AR), Hydrochloric acid (HCl, 37%), oxalic acid ($H_2C_2O_4$, AR), sulfuric acid (H_2SO_4, 98%), sodium sulfate ($NaSO_4$, AR), sodium hydroxide (NaOH, AR), phenol (C_6H_6O, AR) and ultrapure water.

2.1.2 Pretreatment of the Ti substrates

The purpose of the pretreatment of the Ti substrates is to clean its surface and increase roughness to enhance the surface area.[2] Ti plates with a dimension of 3 cm × 3 cm were used as the substrates for all electrodes. Firstly, the Ti plates were polished using sand-blasting machine, and then degreased in a 40 % NaOH solution at 90 °C for 2 h before etched in 10 % boiling oxalic acid at 95 °C for 1 h followed by thorough washing with ultrapure water. Finally, these Ti plates were stored in ethanol and dried with nitrogen blowing before use.

2.1.3 Preparation of the Ti/Sb-SnO_2 electrode

The electrode preparation method is the same as the previous study. The precursor solution was a mixture of $SnCl_2{\cdot}2H_2O$ and $SbCl_3$ (6 at.% relative to Sn) using alcohol (10 ml) and small amount (2 ml) of concentrated hydrochloric acid (37%) as solvents. The concentration of the entire Sn solution is 0.5 mol/l. The precursor solution was then brushed on Ti plates evenly. Then the electrodes were dried at 110 ° C for 5 minutes to evaporate the solvent and baked in a muffle furnace at 550 °C for 20 minutes. This procedure was repeated for 15 times. Finally, the electrodes were annealed at 550 °C for 1 h.

2.1.4 Preparation of Ti/Pt-Sb-SnO2 electrode

For the Ti/Pt-Sb-SnO_2 electrode, $SnCl_4{\cdot}5H_2O$, $SbCl_3$ (6 at.% relative to Sn) and $H_2PtCl_6{\cdot}6H_2O$ (1 at.% relative to Sn) were chosen to prepare the precursor using alcohol (10 ml) and small amount of concentrated (37 %) hydrochloric acid (2 ml) as solvents. The precursor solution was then brushed on Ti plates evenly. Then the electrodes were dried at 110 °C for 5 minutes to evaporate the solvent and baked in a muffle furnace at 550 °C for 20 minutes. This procedure was repeated for 15 times. Finally, the electrodes were annealed at 550 °C for 1 h.

2.2 Characterization of the electrodes

2.2.1 Physical and electrochemical characterization

The morphologies of prepared electrodes were characterized by scanning electron microscopy (SEM, S4800, Hitachi, Japan), equipped with an electron energy-dispersive X-ray spectroscopy (EDX, Hitachi, Japan) for elements test. X-ray photoelectron spectroscope (XPS) was performed to analyze the composition and chemical state of the surface elements (Al Kα radiation, hν=1486.6 eV; Thermo ESCALAB 250Xi, USA). Then the crystal structures were measured by the X-ray diffraction analysis (XRD, XRD-6000, Shimadzu, Japan) using a diffractometer with Cu Kα radiation (λ=0.154 nm) and working at 30 kV/40 mA. The diffraction patterns were collected in the range of 2θ=20-80° at a rate of 5 °/min. Electrochemical experiments were performed in a three-electrode cell recorded by an electrochemical workstation (CHI600E). The effective area of electrodes were polished to 1.0 cm × 1.0 cm, which were employed as working electrodes. The platinum foil (2.5 cm × 2.5 cm) is used as the counter electrode. Meanwhile the saturated Ag/AgCl served as the reference electrode. A Na_2SO_4 solution of 0.25 M was chosen as the electrolyte for both linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The LSV measurement was performed at a sweep rate of 100 $mV{\cdot}s^{-1}$ over the potential range from 0 V to 3 V. The EIS measurement was carried out at an initial potential of 2.2 V with a range of 10^5 Hz to 10^{-2} Hz and an amplitude signal of 5 mV. Then the EIS results were fitted using the ZView program. Finally, the accelerated service life tests were performed by anodic polarization of the prepared electrodes at 100 $mA{\cdot}cm^{-2}$ in 1M H_2SO_4 electrolyte solution at room temperature. The accelerated life of the electrodes was defined as the duration from the beginning of the test to the time at which the cell potential increased by 10 V in 1M H_2SO_4 solution.[9,32,38,39] In all electrode electrochemical tests, the area of the electrodes dipped into the solution in our study is 1.0 cm × 1.0 cm.

2.2.2 Phenol electro-catalytic degradation

The electrochemical degradation of phenol was conducted in an electrochemical workstation (CHI600E) system with effective electrolyte volumes of 100 ml. The electrodes, prepared as described above, served as the anodes (the active area was 2 cm×3 cm), while a stainless steel plate (3 cm × 3 cm) was used as the cathode. The anode and cathode were separated by a 2 cm gap. The volume of simulated wastewater was 100 ml with an initial concentration of 100mg/l phenol. A Na_2SO_4 solution (0.25 mol/l) was used as the supporting electrolyte. The simulated phenol wastewater was electrochemical degraded at 20 $mA{\cdot}cm^{-2}$. Then samples were extracted by 0.2 ml at regular time interval of 30 min to analyze the variation of chemical oxygen demand (COD).

2.2.3 Analysis methods

COD test was used to determinate the current efficiency for the anodic oxidation of phenol by using a COD Analyzer (DR6000 and DRB200). The samples were extracted by 0.2 ml at same time interval of 30 min to analyze the variation of COD. Then the instantaneous current efficiency (ICE) was calculated based on the COD results representing the ratio of the current effectively used in the degradation of phenol at a given time to the applied current and following the equation:

$$ICE = \frac{(COD_t - COD_{t+\Delta t})}{8I\Delta t} FV \times 100\% \qquad (1)$$

where COD_t and $COD_{t+\Delta t}$ are the experimental values of phenol at times t and t+△t ($g{\cdot}l^{-1}$), I is the electrolysis current (A), t is the electrolysis time (s), F is the Faraday's constant (96485 $c{\cdot}mol^{-1}$ electrons) and V is the volume of the Eq.(1). The instantaneous current efficiency (ICE) of phenol degradation was calculated at different electrolysis time.[15,18,25,47]

3. Results and discussion

3.1 Physical characterization of the prepared Ti/Sb-SnO_2-based electrodes

Fig. 1 showed the SEM images of the Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes. As is shown in Fig. 1a, Ti/Sb-SnO_2 electrode shows a typical "cracked-mud" structure with wide and deep cracks. This structure is typical of metal oxide coatings obtained by the thermal decomposition process, which could happen during the cooling of the electrode to room temperature or due to the different thermal expansion coefficients between the active coating and the Ti substrate or during heating stages due to the solvent evaporation.[6,38-39,48,50] This will cause thermal stress and reduce the bonding force, leading to cracking of the active coating and ultimately

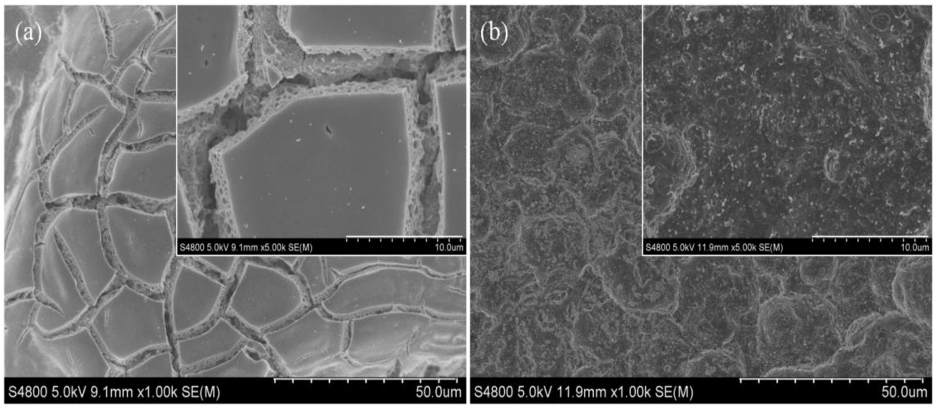

Fig. 1 SEM images: (a) the Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes.

deactivation of the electrode.

In comparison, the surface of electrode changed significantly after the incorporation of Pt. The Ti/Pt-Sb-SnO_2 electrode showed a smooth and homogeneous surface without any obvious cracks due to the compacting effect of Pt, as it has been previously observed.[45,49,51,53] This can block the infiltration of electrolyte and the generation of bubbles to protect Ti substrate, thereby effectively prevent the formation of nonconductive TiO_2 layer and the shedding of the active layer.

Some irregular structures characteristic of Ti/Pt-Sb-SnO_2 can be seen in the inset of Fig. 2a, which greatly increases the electrode surface area. In addition, numerous small grains were also observed with uniform distribution on the surface of the Ti/Pt-Sb-SnO_2 electrodes (Fig. 2). All these changes may improve the electro-catalytic ability, conductivity and service lifetime of electrodes, effectively.[3,26,30] Moreover, the small nanoparticles could be used as building blocks to construct electromagnetic composites, which has potential application in electronic device too.[55-56]

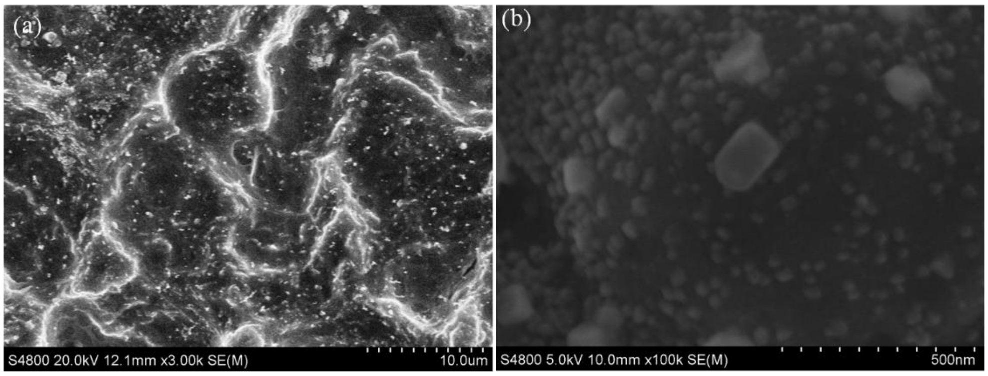

Fig. 2. SEM images of fresh Ti/Pt-Sb-SnO_2 electrodes.

Table 1. The surface compositions of Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes obtained by EDX.

Electrodes	Sn(at.%)	Sb(at.%)	O(at.%)	Ti(at.%)	Pt(at.%)
Ti/Sb-SnO_2	3.21	0.18	58.83	37.78	-
Ti/Pt-Sb-SnO_2	20.33	1.22	69.73	8.63	0.09

To further characterize the surface characterization of the electrode, EDX analysis was performed. Table 1 shows the EDX results of the both electrodes, the active layer of both electrodes mainly consists of Sn, Sb, O, Pt and Ti elements. Compared to Ti/Sb-SnO_2, the obvious reduction in Ti content of Ti/Pt-Sb-SnO_2 also demonstrated that the Ti/Pt-Sb-SnO_2 electrode has the better coverage of the Ti substrate, which is consistent with the SEM results.

Fig. 3 shows the XRD results of the Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes. The pattern of the both electrodes is very

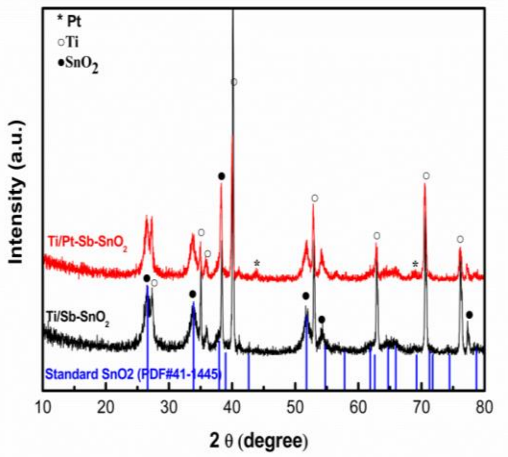

Fig. 3. XRD patterns of the Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes.

similar with sharp peaks corresponding to the tetragonal rutile structure of SnO_2 phase (JCPDS:41-1445) and Ti diffraction peaks, indicating that the introduction of Pt does not change the major crystal structure. In addition, the Ti peak diffraction intensity decreases after Pt doping, indicating that the Ti-based surface is better uniformly covered, which is consistent with the SEM test results. In addition, from the results of EDX, we confirm the existence of Sb element. But there are no diffraction peaks related to Sb metal oxides, which may be due to either the low doping level or the incorporation of the Sb ions into the SnO_2 lattice in the form of interstitial, replacement, or being dispersed in the middle of the SnO_2 lattice.[37,41]

Additionally, the peaks associated with the presence of the Pt metallic phase can be observed, specifically the reflections corresponding to the (200) and (220) plane. And no other peaks corresponding to Pt metal oxide phases can be observed. Similar results were obtained by other researchers.[48,52] The lattice parameters of the electrode calculated by Bragg's formula are listed in Table 2. All the three parameters transformed slightly due to the introduction of Pt ions. The most reasonable explanation of this kind of the lattice shrinkage was that Pt ions entered the unit cell of the SnO_2. The corresponding lattice parameters and the volume of the unit cell of Ti/Pt-Sb-SnO_2 electrode were lower owing to the introduction of Pt into the SnO_2 crystal lattice.[39]

Table 2. Lattice parameters and diameters of Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes obtained by XRD.

Electrodes	lattice parameters(Å)			volume(Å^3)
	a	b	c	V
Ti/Sb-SnO_2	4.69256	4.69256	3.27299	71.41
Ti/Pt-Sb-SnO_2	4.69188	4.69188	3.24185	71.34

3.2 Electrochemical measurements

3.2.1 Linear sweep voltammetry

The OEP value is one of the important parameters d to assess the electrochemical performance of the electrodes. As is reported, a higher OEP value is crucial and desirable.[4,33] During the electro-catalytic degradation process, besides the main electro-catalytic reaction, OER as a major side effect also occurs causing a power loss and reducing the overall current efficiency. The specific electrochemical oxidation process can be expressed by the following reactions.[19]

$$SnO_2 + H_2O \rightarrow SnO_2(\cdot OH)_x + xH^+ + xe^- \qquad (2)$$

$$SnO_2(\cdot OH)_x + R \rightarrow SnO_2 + CO_2 + xH^+ + xe^- \qquad (3)$$

$$SnO_2(\cdot OH)_x \rightarrow SnO_2 + \frac{x}{2}O_2 + xH^+ + xe^- \qquad (4)$$

where *R* represents the organic pollutants. Firstly, H_2O molecules dissociate and form·OH_{ads} (mainly $SnO_2(\cdot OH)_x$), as shown in Eq.(2). Then, the $SnO_2(\cdot OH)_x$ can not only oxidize the organic compounds (Eq.(3)), but also dissociate to form O_2 (the so called OER, Eq.(4)). The two reactions of electrochemical oxidation of organics and OER compete with each other, which leads to the decrease of current efficiency. In this way, the higher the OEP value, the more effective the occurrence of OER side reactions can be inhibited. Therefore, it is an important index to evaluate the electrochemical performance of electrodes.[19,23,27-29,35]

Fig. 4 shows the LSV of the as-prepared Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes. The OEP values were 2.45 eV and 2.10 eV (vs. SCE) for the Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes, respectively, indicating that doping Pt decrease the OEP of electrode slightly. But, the higher current response of Ti/Pt-Sb-SnO_2 electrode indicates that the charge transfer resistance of the electrode is smaller (as shown in Fig. 4), which will be discussed in EIS test.

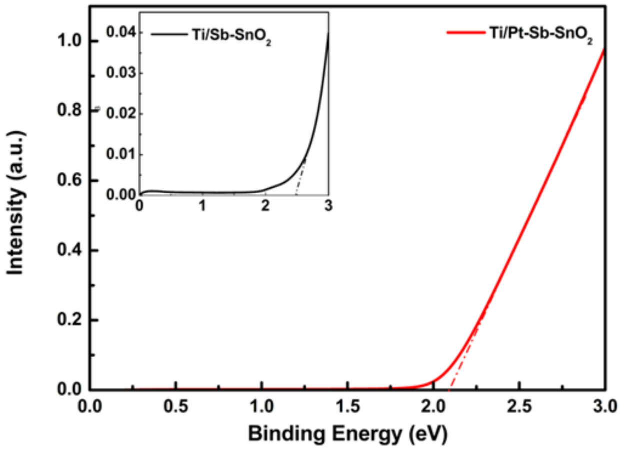

Fig. 4. Linear sweep voltammetry of Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes.

3.2.2 EIS analysis

To investigate the interfacial electrochemical properties of the Ti/Pt-Sb-SnO_2 electrodes between electrodes and solution, the EIS measurements were conducted. Fig. 5 depicts the EIS spectra and equivalent circuit for both electrodes. All the plots are similar, indicating that the two electrodes have similar electrochemical behavior. The introduction of Pt effectively reduces the electrochemical resistance of the Ti/Sb-SnO_2 electrode, mainly due to the excellent conductivity of Pt. The equivalent circuit $R_s(R_{ct}CPE)$, which is often used to analyze the EIS spectra in detail, is used for fitting the impedance spectra by ZView software in our experiment, as shown in Fig. 5b. In the corresponding equivalent circuit, R_s represents the solution resistance between the reference electrode and the prepared electrode; CPE is the constant phase element; R_{ct} represents the charge transfer resistance between the oxide and the solution interface, which mainly reflects the electro-catalytic activity of the electrode to phenol.[3,17,57] According to the fitting results, the arc diameter corresponding to R_{ct} of Ti/Pt-Sb-SnO_2 electrode is smaller than that of Ti/Sb-SnO_2 electrode, indicating that Ti/Pt-Sb- SnO_2 electrode had the lowest charge transfer resistance and the superior conductivity, which facilitates the electro-catalytic reaction rate and phenol removal. And hence the energy loss and cell potential are also expected to be reduced which would be beneficial for economic rationality of water treatment process. Despite of the slight lower OEP of Ti/Pt-Sb-SnO_2, the significantly smaller charge transfer resistance still guarantees its superior electrochemical activity.

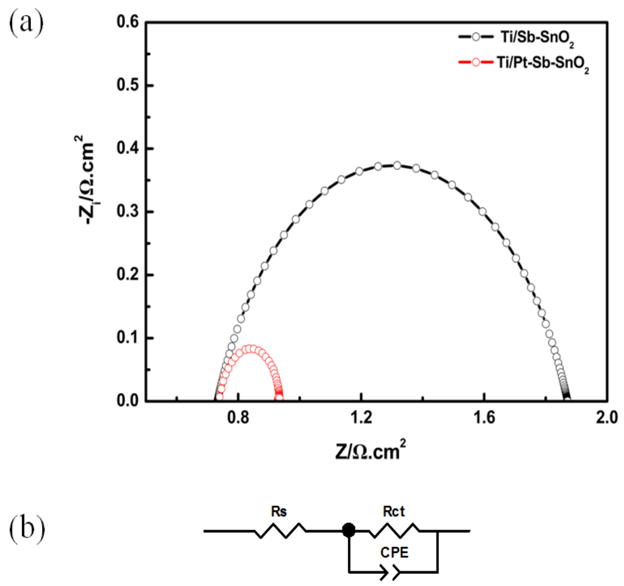

Fig. 5 (a) Impedance Nyquist plots and (b) equivalent circuit of Ti/Sb-SnO_2 and Ti/Pt- Sb-SnO_2 electrodes.

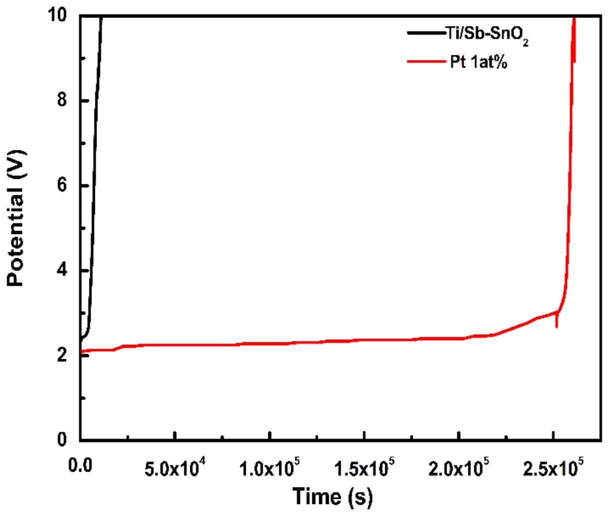

Fig. 6 Accelerated lifetime measurements of the Ti/Sb-SnO_2 and Ti/Pt-Sb-SnO_2 electrodes.

3.2.3 Electrode stability

The stability is another vital factor for evaluating the electrode quality. The main problem for Ti/Sb-SnO_2 electrodes is their poor stability. Fig. 6 shows the accelerated life test results. The accelerated lifetime of the Ti/Sb-SnO_2 is about 3 h, while that of Ti/Pt-Sb-SnO_2 prolong the lifetime almost to 73 h, which is almost 24 times longer than that of Ti/Sb-SnO_2. The reason for the improved life could relate to the uniform coating structure with better coverage on Ti substrate. Furthermore, the introduction of Pt promotes the conductivity of electrodes and decreased the electrochemical impedance, which lower the potential of the electrode, and thereby the Ti/Pt-Sb-SnO_2 electrode exhibited prolonged durability, demonstrating the significant role of the Pt enhanced the stability of electrode.

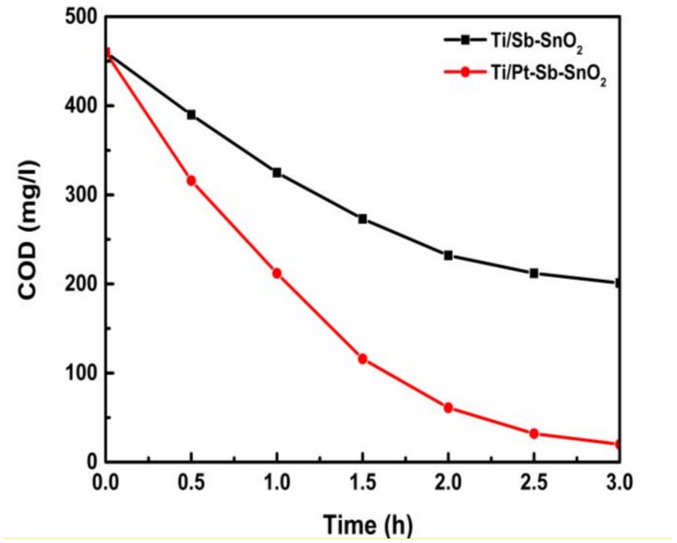

Fig. 7 Variations of COD with electrolysis time corresponding to the following anodes.

3.3 The electrochemical oxidation of phenol

In this study, phenol was used as the target pollutant for evaluating the electro-catalytic oxidation efficiency of the electrodes. Because the electro-catalytic of phenol might generate different byproducts, such as quinine, p-benzoquinone, hydroquinone, maleic acid, fumaric acid and so on, which are likely to be more recalcitrant to be degraded than phenol, the analysis of COD removal is very important to study the performance of phenol oxidation and can provide a better understanding of the electro-catalytic ability of an electrode.[47,50,53,54] The electro-catalytic of phenol is a complicated process. Firstly, phenol is decomposed into the aromatic compounds such as benzoquinone or hydroquinone. Then, the aromatic ring cracks and a series of carboxylic acids are produced. Lastly, the carboxylic acids are almost completely mineralized into CO_2 and H_2O. Simultaneously, the polymeric products may accumulate and be likely more recalcitrant to be degraded than phenol, which causes the solutions to exhibit color changes during the electrolysis process. For the Ti/Pt-Sb-SnO_2 electrode, the liquid firstly turned to yellow, then the yellow color began to fade, and the color had almost disappeared about 3 h before the COD was completely removed. It is believed that the yellowing of the phenol solution is caused by the production of benzoquinone, which is produced by phenol oxidation.[5,54] However, for Ti/Sb-SnO_2, the yellow color did not completely disappear after 3h, which was consistent with the results discussed above. As shown in Fig. 7, the COD removals of phenol by the both electrodes were compared mainly to further evaluate the effect of the Pt doping on the electro-catalytic ability of the electrode. The COD was removed more rapidly by the Ti/Pt-Sb-SnO_2 electrode than the Ti/Sb-SnO_2 electrode. After 3 hrs, 95.56% (Ti/Pt-Sb-SnO_2) and 56.31% (Ti/Sb-SnO_2) of COD removal were achieved, respectively. In addition, the ICE is another evaluation of the electrodes' electrochemical degradation performance for the pollutants representing the ratio of the current effectively employed in the degradation at a given time to the applied current.

The ICE of the electro-catalytic oxidation of the two electrodes is shown in Fig. 8. The ICE on Ti/Pt-Sb-SnO$_2$ is always higher than that on Ti/Sb-SnO$_2$, indicating that theTi/Pt-Sb-SnO$_2$ electrode has the higher current efficiency, which is in accordance with the COD reduction. What's more, the ICE value is dramatically decreased with time, which may be attributed to the loss of coating, the increase of impedance between electrolyte and electrode, the formation of refractory organic intermediates toward anodic oxidation, and the OER inhibiting the mass transport of organics to electrode surface and competing with the phenol degradation.[24,47] As the time passed, the concentrations of byproducts increased rapidly, and the OH radicals were captured by both unreacted phenol as well as these byproducts, resulting in a slow degradation rate.[47,50,53] After 3 h the ICE of Ti/Pt-Sb-SnO$_2$ decreased to 6.71%, still keeping higher to Ti/Sb-SnO$_2$.

All the above results signify that Ti/Pt-Sb-SnO$_2$ electrode possesses better performance of over Ti/Sb-SnO$_2$ for mineralizing the phenol. And we will conduct a detailed study in the next work.

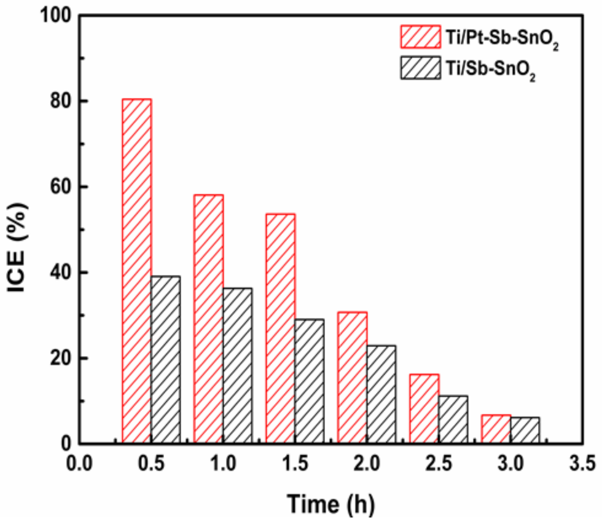

Fig. 8 Instantaneous current efficiency (ICE) with time on the different electrodes.

4. Conclusion

In this paper, Ti/Sb-SnO$_2$ and Ti/Pt-Sb-SnO$_2$ is prepared by the sample dip-coating technique. The structural characteristics and compositions of the electrodes are investigated by SEM, EDX and XRD. The electrochemical and electro-catalytic degradation properties of the electrodes were also studied. The main conclusions of our work can be summarized in the following points:

- SEM results have shown that the presence of Pt in the Ti/Sb-SnO$_2$ anodes leads to a more compact morphology. This change may be due to the compacting effect of Pt.
- Ti/Pt-Sb-SnO$_2$ electrode showed a lower R_{ct} and better electro-catalytic activity.
- The service life of Ti/Pt-Sb-SnO$_2$ anodes is about 73 h in a H_2SO_4 aqueous solution as electrolyte. It is nearly 24 time longer than that of Ti/Sb-SnO$_2$ electrode.
- Ti/Pt-Sb-SnO$_2$ electrode was most effective in phenol and the COD removal, and the COD removals almost reached to 95.56% after 3 hours.

Considering all the results above and in terms of energy consumption and stability, the addition of Pt was mainly responsible for improving the catalytic activity and service time of Ti/Sb-SnO$_2$ anode. The Ti/Pt-Sb-SnO$_2$ electrode may be a kind of very promising electrode.

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Supporting information

Not Applicable.

Conflict of interest

There are no conflicts to declare.

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